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By: Judith Muzyk Date: January 12, 2004
Judith Muzyk

Docket No.: 9913/9-1802

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Johan C. FITTER Conf. 9478
Serial No.: 09/739,483 Group Art Unit: 1745
Filing Date: December 18, 2003 Examiner: G. Cantelmo
For: AN ELECTROCHEMICAL CELL

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR 1.132

Sir:

1. I, Johan C. Fitter, am the sole inventor of the subject matter claimed in the above referenced application.
2. I have reviewed the office action dated July 25, 2003, as well as the translated portions of JP 10-302785A, JP50-091728 and JP01-267965A.
3. My invention is directed to a rechargeable electrochemical cell which is subjected to multiple charging and discharging cycles, each charging cycle having a charging portion corresponding to a gassing charge where gas is generated and a charging portion below the gassing charge. I have found that the presence of charge dependant impeding means disposed in the electrolyte and having a constituent bonded to the negative electrodes of the electrochemical

cell forms a barrier for impeding the gassing charge, the charge dependant impeding means being activated by the charging portion corresponding to the gassing charge and being deactivated by the charging portion below the gassing charge to limit gas generation when activated, but having no charge limiting effect below the gassing charge, and further, having substantially no effect during the discharge cycle.

2. That these means are therefore "charge dependant" is of particular importance, as this allows charging and discharging to proceed normally, activation of the impeding effect only occurring when the gassing charge level is reached, as described in the patent specification, pg. 21 line 21 to pg. 22, line 2, with reference to Figures 4 and 5. The ability of the means to be so "charge dependant" is believed to be related to the specific type of attachment or bonding of the means to the negative electrode.

3. For example, as shown in Figure 6, the means comprise quaternary ammonium compounds 38 with "heads" attached to the electrode surface, and "tails" extending into the electrolyte, thereby impeding ion transport, and so the orientation is believed to be necessary to obtain the charge dependent impeding effect.

4. I have enclosed as Exhibit 1 portions of chapter 10 from the book "Fundamentals of Electrochemical Deposition, entitled "Effect of Additives".

5. Pages 171-173 describe adsorbate molecular orientation at an electrode surface. On page 172 there is described a change from a parallel or vertical orientation, with a constituent bonded to an electrode surface, to an edgewise or horizontal orientation, where the entire molecule is attached or bonded to the electrode surface, of an adsorbate molecule. Changes in adsorbate concentration can result in reorientation, the parallel orientation occurring at low concentrations,

and there then being an irreversible reorientation to the edgewise configuration occurring as the concentration is increased. Figures 10.5 and 10.6 illustrate the molecular orientation of various molecules, and the packing density for parallel versus edgewise orientation. The parallel or vertical orientation is similar to the type of bonding or attachment of the charge dependant impeding means to the negative electrodes shown in my Figure 6.

6. I have described in the specification how the concentration of the charge dependant impeding means from as little as 5 mg/l, up to about 1500 mg/l, functions well in accordance with my invention. I have now conducted a test using dodecyldimethylbenzylammonium chloride, at about 1 percent concentration, in a lead acid battery and found that the impeding means are no longer "charge dependant" and remain activated, affecting both the discharge cycle, as the cell loses voltage faster and the charge cycle, as the cell gains voltage faster. I believe this is due to a reorientation to the edgewise configuration caused by the higher concentration.

7. According to JP50-091728, a concentration of 3% of the dodecyldimethylbenzylammonium chloride was added to a Ni-Zn Alkaline battery electrolyte (30% KOH), and at such a concentration, in my opinion, charge dependant impeding means are not present, since the orientation would be edgewise, and remain in an activated state during any charging and discharging cycles.

8. As to JP10-302785A, in my opinion, the inclusion of a fatty acid in a paste used to produce an anode could not provide the attachment orientation necessary to providing charge dependant impeding means, and it appears this is demonstrated by the significant effects in the discharge cycle referenced in paragraph 011, and shown in Table 3.

9. As to JP01-267965, this relates solely to suppressing lead metal disassociation, that is, the

amount of lead ion present in the electrolyte. While it is not perfectly clear, it appears that the table included in the patent shows the proportional decrease in lead dissolved, from 45.2 mg/l, down to 1.52 mg/l as the ammonium concentration is increased from 0.5 up to 40 % wt., the lowest metal disassociation occurring over 25%. With these concentrations, charge dependant impeding means are clearly not found in JP '965.

10. In none of these documents is there any suggestion that a particular orientation could provide activatable impeding means to reduce gassing, as found in my claimed invention. Further, the concentrations used render it a certainty that such an orientation was not inherent in any of the examples discussed in the cited documents.

11. I believe the inventive electrochemical cell as presented in the claims of my patent application is distinguishable from the prior art as these patents do not provide "charge dependant impeding means" as required by these claims, and one skilled in this art would be particularly surprised that such distinctly beneficial effects could be achieved, even when compared to the same compounds, when the described bonding or attachment of a constituent is provided.

I, the undersigned inventor, further declare that all statements herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further, and that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date:

JANUARY 12, 2004

Johan C. Fitter, Inventor



FUNDAMENTALS OF ELECTROCHEMICAL DEPOSITION

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Reaction (9.14) is a very important displacement deposition reaction in the printed circuit industry. It is used to help the soldering capability of copper.

9.5. KINETICS AND MECHANISM

The kinetics and mechanisms of the displacement deposition of Cu on a Zn substrate in alkaline media was studied by Massee and Piron (5). They determined that at the beginning of the deposition process, the rate is controlled by activation. The activation control mechanism changes to diffusion control when the copper covers enough of the Zn surface to facilitate further deposition of copper. This double mechanism can explain the kinetic behavior of the deposition process.

The mechanisms of the crystal building process of Cu on Fe and Al substrates were studied employing transmission and scanning electron microscopy (1). These studies showed that a nucleation-coalescence growth mechanism (Chapter 7, Section 7.10) holds for the Cu/Fe system and that a displacement deposition of Cu on Fe results in a continuous deposit. A different nucleation-growth model was observed in the case of the Cu/Al system. Displacement deposition of Cu on Al substrate starts with formation of isolated nuclei and clusters of Cu. This mechanism results in the development of dendritic structures.

The properties of deposits may be controlled by changing the kinetics of the deposition and the mechanism of crystallization. One way to achieve this is by complexing the depositing ions, as stated above.

REFERENCES AND FURTHER READING

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3. M. Paunovic and C. H. Ting, in *Electroless Deposition of Metals and Alloys*, M. Paunovic and I. Ohno, eds., PV 88-12, The Electrochemical Society, Pennington, NJ, 1988.
4. C. H. Ting, in *Electroless Deposition of Metals and Alloys*, M. Paunovic and I. Ohno, eds., PV 88-12, The Electrochemical Society, Pennington, NJ, 1988.
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6. G. J. Norga, M. Platzer, K. A. Black, A. J. Reddy, J. Michel, and L. C. Kimerling, *J. Electrochem. Soc.* **144**, 2801 (1997).

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Effect of Additives

10.1. INTRODUCTION

Most solutions used in electrodeposition of metals and alloys contain one or more inorganic or organic additives that have specific functions in the deposition process. These additives affect deposition and crystal building processes as adsorbates at the surface of the cathode. Thus, in this chapter we first describe adsorption and the factors that determine adsorbate-surface interaction. There are two sets of factors that determine adsorption: substrate and adsorbate factors. Substrate factors include electron density, *d*-band location, and the shape of substrate electronic orbitals. Adsorbate factors include electronegativity and the shape of adsorbate orbitals.

After discussing adsorption, we discuss the effects of additives on the kinetic parameters of the deposition process and on the elementary processes of crystal growth.

10.2. ADSORPTION

Chemisorption and Physisorption. One classification of adsorption phenomena is based on the adsorption energy: the energy of the adsorbate-surface interaction. In this classification there are two basic types of adsorption: chemisorption (an abbreviation of *chemical adsorption*) and physisorption (an abbreviation of *physical adsorption*). In chemisorption the chemical attractive forces of adsorption are acting between surface and adsorbate (usually covalent bonds). Thus, there is a chemical combination between the substrate and the adsorbate where electrons are shared and/or transferred. New electronic configurations are formed by this sharing of electrons. In physisorption the physical forces of adsorption, van der Waals or pure electrostatic forces, operate between the surface and the adsorbate; there is no electron transfer and no electron sharing.

Adsorption energy for chemisorbed species is greater than that for physisorbed species. Typical values for chemisorption are in the range of 20–100 kcal/mol and for physisorption, in the range of 5 kcal/mol.

The difference between physisorption and chemisorption can be explained using a potential-energy diagram. The potential-energy diagram for physisorption and chemisorption of an A–A molecule (e.g., H₂) is shown in Figure 10.1. Curve P in

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EFFECT OF ADDITIVES

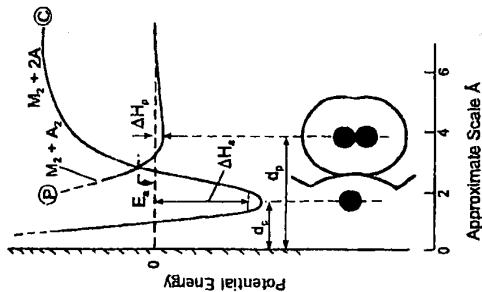


Figure 10.1. The potential-energy diagram for physisorption and chemisorption of an A-A molecule.

Figure 10.1 gives the potential energy of the molecule A_2 for cases in which only physical forces of attraction are operating. It is seen that as the molecule approaches the surface, its energy falls as it becomes physisorbed. The minimum of this curve represents the equilibrium state for the physisorbed molecule. The potential well q_p (ΔH_p), the heat of adsorption for the physisorbed molecule, is relatively shallow and is due to long-range forces (e.g., van der Waals forces) so that the equilibrium distance from the surface (d_p) is relatively large. It is located at the sum of the van der Waals radii for the surface atom and the adsorbate A_2 molecule. An attempt to decrease the distance of separation below the equilibrium value leads to gradually increasing repulsion. Curve C corresponds to the interaction of two A atoms with the surface. The minimum of this curve represents the equilibrium state for chemisorbed atoms A. The minimum is deeper and at a smaller distance (d_c) than the one for physisorption (d_p). The two curves (P and C, Fig. 10.1) cross, and the adsorbate can pass from the first to the second. The transition from physisorption to chemisorption occurs at the crossing point of curves P and C. The energy at this point is the activation energy E_a , which is the excess of energy of that for the separated metal and A_2 molecule. It is the activation energy for the transition from physical to chemical adsorption. Figure 10.1 shows that chemisorption in this case involves dissociation of physisorbed molecules.

Adsorption Equilibrium. Since the additive is not used up in many cases of electrodeposition in the presence of an additive (the additive is not incorporated in the deposit), one can conclude that the adsorption equilibrium is dynamic. In a dynamic adsorption equilibrium state the adsorbed molecules are continually desorbing at a rate equal to the rate at which dissolved molecules from the solution

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become adsorbed. If the rates of the adsorption and desorption processes are high and of the same order of magnitude as that of the cathodic deposition process, then no incorporation, or entrapment, of additives in the deposit will occur. However, if they are much smaller, additive molecules will be entrapped in the deposit via propagating steps (growing crystallites). Thus, at a current density higher than the optimum value, additives (brighteners or levelers) will be incorporated into the deposit. This incorporation can result in poor quality of the resulting deposit.

Adsorption Isotherms. Adsorption isotherms describe the relationship between the coverage θ of the surface by the adsorbate and the concentration of the adsorbate in the bulk solution, c^b , at a given temperature. The surface coverage θ is defined as

$$\theta = \frac{N_{\text{occ}}}{N} \quad (10.1)$$

where N_{occ} and N are the number of adsorption sites occupied and the total number of adsorption sites available, respectively. From this equation it follows that $N\theta = N_{\text{occ}}$ = number of adsorption sites occupied, and $N - N_{\text{occ}} = N(1 - \theta)$ = number of vacant sites.

The relationship $\theta = f(c^b)$ can be derived from a kinetic model assuming that the rate of adsorption r_a is proportional to the number of vacant sites $N(1 - \theta)$ and also to the bulk solution concentration c^b

$$r_a = k_a N(1 - \theta) c^b \quad (10.2)$$

and that the rate of desorption r_d is proportional to the number of adsorption sites occupied, $N\theta$

$$r_d = k_d N\theta \quad (10.3)$$

where k_a and k_d are adsorption and desorption rate constraints, respectively. At dynamic equilibrium $r_a = r_d$ and

$$k_a N(1 - \theta) c^b = k_d N\theta \quad (10.4)$$

Solving for θ , one obtains the Langmuir isotherm (Section 10.3, Ref.1)

$$\theta = \frac{Kc^b}{(1 + Kc^b)} \quad (10.5)$$

where $K = k_a/k_d$ is the adsorption equilibrium constant.

The Langmuir isotherm is based on the simplest model that involves the following assumptions: (1) the adsorption energy of all sites is the same and is unaffected by adsorption on neighboring sites, (2) the adsorption is immobile, (3) each site accommodates only one adsorbed particle, and (4) adsorbed atoms (molecules) do not interact with each other. Figure 10.2a shows that the Langmuir-type isotherm for

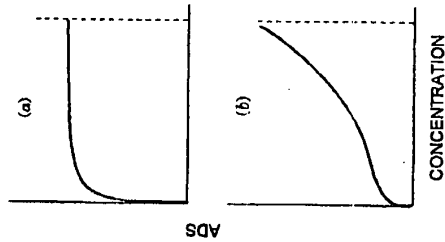


Figure 10.2. Types of adsorption isotherms: (a) Langmuir type; (b) physisorption, multilayer.

chemisorption has a limiting adsorption that corresponds to a monolayer coverage. In contrast, isotherm for a physisorption (Fig. 10.2b) does not show a saturation plateau but indicates a multilayer formation.

Equation (10.5) is valid for cases where there is no dissociation on adsorption. However, in many cases chemisorption is dissociative, involving, for example, adsorption of hydrogen (H_2). In these cases the chemisorption process can be formulated as shown in Figure 10.3. If the adsorbed molecule dissociates into n fragments, then the Langmuir isotherm has the form

$$\theta = \frac{K(c^b)^{1/n}}{1 + K(c^b)^{1/n}} \quad (10.6)$$

If a molecule is being adsorbed on m sites on the surface, without dissociation, the following equation holds:

$$\frac{\theta}{(1 - \theta)^m} = Kc^b \quad (10.7)$$

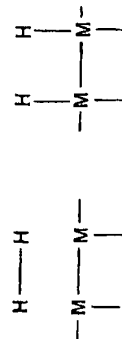


Figure 10.3. Dissociative adsorption of H_2 molecule.

Adsorption isotherms for n -decylamine on Ni, Fe, Cu, Pb, and Pt at the potential of maximum adsorption are shown in Figure 10.4. It is seen that a limiting coverage is approached in each case except on Pt, where multilayer formation occurs. The coverage θ in this case is defined as

$$\theta = \frac{\Gamma}{\Gamma_s} \quad (10.8)$$

where Γ is the surface concentration of adsorbate (mol/cm^2) and Γ_s is the saturation coverage of electrode by adsorbate (or Γ_{max}). In this case Γ_s is $7.9 \times 10^{-10} \text{ mol}/\text{cm}^2$ (Γ_m in Fig. 10.4). Thus, a very small amount of material is involved in adsorption. This case is of interest since this small amount of adsorbent can influence the type of deposit, as is shown in Section 10.5.

Simultaneous Adsorption of Two or More Species. If there are N different additives adsorbed at the electrode, the total surface coverage θ_T is given by

$$\theta_T = \theta_1 + \theta_2 + \theta_3 + \dots + \theta_N \quad (10.9)$$

where $\theta_1, \theta_2, \theta_3, \dots, \theta_N$ is the surface coverage of additive $A_1, A_2, A_3, \dots, A_N$, respectively.

Adsorbate Molecular Orientation at Electrode Surface. Adsorption of some molecules from solution produces an oriented adsorbed layer. For example, nicotinic acid (NA, or 3-pyridinecarboxylic acid, "niacin" or vitamin B_3) is attached to a Pt(111) surface primarily or even exclusively through the N atom with the ring in a (nearly) vertical orientation (Section 10.3, Ref. 12) (Fig. 10.5a).

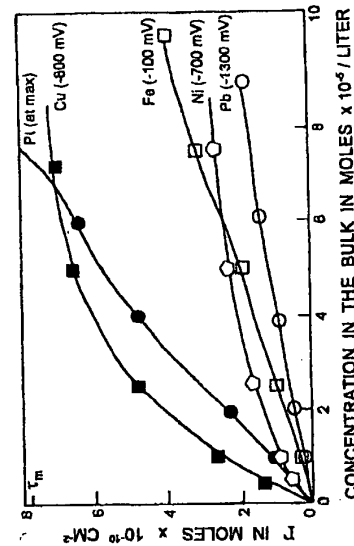


Figure 10.4. Adsorption isotherms for n -decylamine on Ni, Fe, Cu, Pb, and Pt at the potential of maximum adsorption. (From Ref. 5 in Section 10.3, with permission from the Electrochemical Society.)

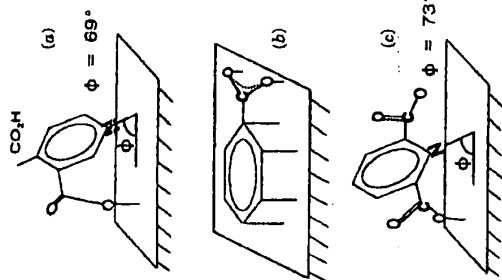


Figure 10.5. Adsorbate molecular orientation at the electrode surface: (a) nicotinic acid; (b) benzoic acid; (c) 2,6-pyridinedicarboxylic acid. (From Ref. 12 in Section 10.3, with permission from the American Chemical Society.)

In another example, benzoic acid (BA) is an aromatic compound that orients horizontally at a Pt(111) surface (Fig. 10.5b). This horizontal orientation of adsorbed BA involves coordination of the carboxylic acid to the Pt surface. The coordination depends on surface potential (Section 10.3, Ref. 12). BA adsorbed at negative potentials is coordinated to the Pt through the aromatic ring and (primarily) one carboxylate oxygen; when adsorbed at positive potentials, it is coordinated to the Pt surface through two equivalent oxygens. 2,6-Pyridinedicarboxylic acid (2,6 PDA) adsorbs in a tilted fashion with $\theta = 73^\circ$, as seen in Figure 10.5c. When adsorbed at negative potentials, it is coordinated by one, not both, carboxylates to the Pt surface; in contrast, when adsorbed at positive electrode potentials, it is coordinated by both carboxylates to Pt, each through one oxygen.

Change in adsorbate concentration in solution can also result in orientational changes of molecules on the surface. For example, Soriaga et al. (Section 10.3, Ref. 10) have shown that diphenols and quinones are adsorbed on Pt electrodes with the diphenol or quinonoid ring parallel to the substrate at low concentration and reorient irreversibly to edgewise orientations as the concentration is increased. Figure 10.6 illustrates the way the average area occupied by a single molecule in the adsorbed layer depends on the orientation of the adsorbate on the surface, and how the molecular packing density, expressed in mol/cm^2 , depends on adsorbate molecular orientation. Thus, the adsorbate orientation and orientational transitions are of fundamental and practical interest because of their influence on the kinetics and mechanism of electrochemical deposition.

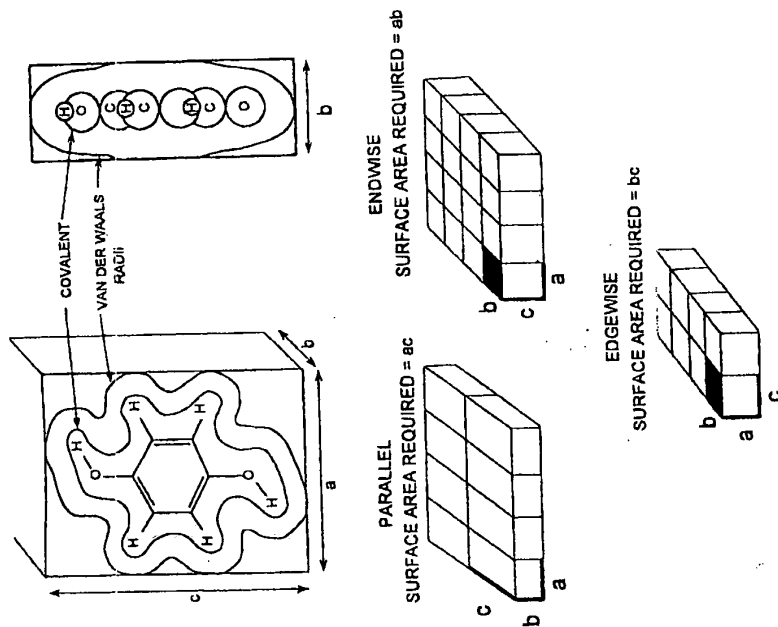


Figure 10.6. The orientation of adsorbate on the surface and the molecular packing density. (From Ref. 10 in Section 10.3, with permission from Elsevier.)

Adsorption of Polymers. The three major characteristics of polymers in the metal-solution interphase, of interest in metal deposition, are polydispersity, large number of configurations, and number of points of attachments. Polymers used as additives (e.g., wetting agents) as prepared are generally polydisperse. Their adsorption has to be treated as a multicomponent system. For good reproducibility in metal deposition, it is important to use relatively limited molecular-weight fractions. A large number of configurations and the number of points of attachment are factors that determine the rate of attainment of adsorption equilibrium.

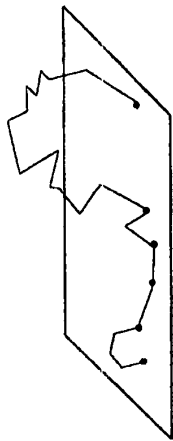


Figure 10.7. Schematic representation of adsorbed polymer.

The shape of flexible polymer molecule in the vicinity of the surface is greatly distorted from the average shape in solution. Adsorbed polymer molecules are attached to the surface by stretches of segments at the surface alternating with loops out of the surface (Fig. 10.7).

10.3. EXPERIMENTAL METHODS FOR STUDY OF ADSORPTION

Potentiodynamic Technique. Adsorption of methanol on Pt in acid solution was studied by Breiter and Gilman (3) using potentiostatic technique. The anodic sweep, with a sweep rate of 800 V/s, was started at rest potential and extended to 2.0 V, with respect to hydrogen reference electrode in the same solution. As shown in Figure 10.8, the current was recorded as a function of potential (time) in the absence (curve A) and in the presence (curve B) of methanol. The increase in the current in curve B is due to oxidation of the adsorbed methanol on the platinum electrode. Thus, the shaded area 2 minus the shaded area 1 (Fig. 10.8) yields the change Q_M (C/cm^2) required for the oxidation of the adsorbed methanol:

$$Q_M = \int_0^{\tau} i_b dt - \int_0^{\tau} i_a dt \quad (10.10)$$

The applicability of this technique is based on four assumptions: (1) the number of coulombs per square centimeter used for the anodic formation of an oxygen layer ($2OH^- = O_{ads} + H_2O + 2e$) and the oxygen evolution during the sweep is the same in either the absence or presence of methanol; (2) the same number of electrons per molecule, independent of the amount of the adsorbed methanol, is used up in the oxidation; (3) the double-layer charging current is the same in the presence or absence of methanol; and (4) the anodic sweep is sufficiently fast (here 800 V/s) such that oxidation of methanol, which diffuses from the bulk solution to the electrode during the sweep, is negligible (i.e., only the adsorbed methanol is oxidized).

Galvanostatic Transient Technique. Breiter (4) measured the adsorption of formic acid (HCOOH) on platinum in the solution of perchloric acid ($HClO_4$) using

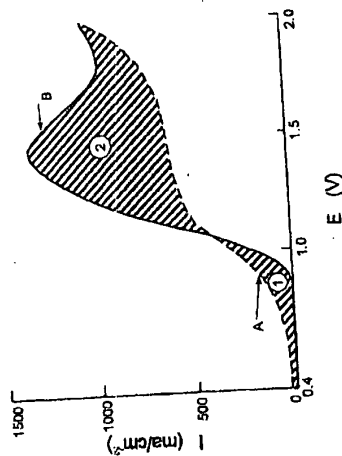


Figure 10.8. Potentiostatic i - E curves with $V = 800$ V/s in $HClO_4 + 1$ M CH_3OH (curve B) and in 1 N $HClO_4$ (curve A) starting from the open-circuit potential. (From Ref. 3, with permission from the Electrochemical Society.)

galvanostatic transient technique. Figure 10.9 shows two anodic galvanostatic transients at 91 mA/cm² on Pt in $HClO_4$ (curve a) and in $HClO_4 + HCOOH$ (curve b). Curve a corresponds to the anodic formation of an oxygen layer (Pt-O) on Pt. The completion of about a monolayer Pt-O is reached at the transition time τ_0 (after the completion of about a monolayer Pt-O corresponds to a simultaneous oxidation of adsorbed HCOOH molecules and the formation of the oxygen layer. A plateau at about 1.0 V results from the oxidation of the adsorbed HCOOH. The transition time τ_F for the oxidation of the adsorbed HCOOH (formic acid) molecules alone is

$$\tau_F = \tau - \tau_0 \quad (10.11)$$

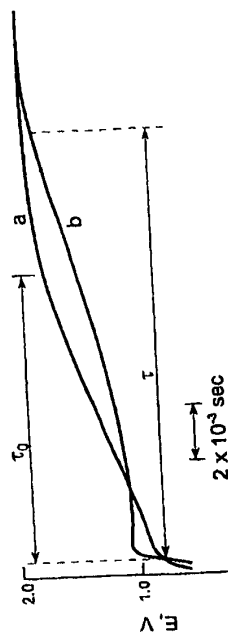


Figure 10.9. Anodic charging curves from 0.4 V during the galvanostatic transients anodic potential sweep at 91 mA/cm² in 1 N $HClO_4$ (curve a) and in 1 N $HClO_4 + HCOOH$ (curve b). (From Ref. 3, with permission from the Electrochemical Society.)

This equation is written assuming that (1) the charging of the double layer requires approximately the same charge Q [number of coulombs per square centimeter (Coul/cm²)] for curves a and b , (2) the number of coulombs per square centimeter for the anodic formation of an oxygen layer on Pt is the same for curves a and b , and (3) oxidation of HCOOH molecules that diffuse to the Pt electrode is negligible since the transition times are short enough (order of 10^{-3} sec). The coverage θ_F of formic acid molecules is given as

$$\theta_F = \frac{\tau_F}{\tau_{Fm}} = \frac{\tau - \tau_0}{\tau_m - \tau_0} \quad (10.12)$$

where τ_{Fm} refers to a monolayer of HCOOH molecules (or, τ_m is the limiting value of τ_F).

Chronopotentiometry. Paunovic and Oechslein (8) measured the adsorption of peptone on lead-tin alloy electrodes using chronopotentiometric and double-layer measurements. This case is different from the previous (adsorption of HCOOH) since peptone is not an electroactive species in the studied conditions, but it only blocks the surface used for the electrodeposition of lead-tin alloys from the solutions containing Sn^{2+} and Pb^{2+} ions. Chronopotentiometric analysis is based on the following principles (7). In the absence of adsorption, the relationship between the transition time τ (for reduction of Sn^{2+} and Pb^{2+} in this case), the bulk concentration c^0 of the substance reacting at the electrode, and the current I is given by the equation

$$\sqrt{\tau} = \frac{nFA\sqrt{\pi D}}{2I} c^0 \quad (10.13)$$

where n is the number of electrons involved in the reaction, F is the Faraday constant, A is the surface area of the electrode, and D is the diffusion coefficient (diffusivity). For a given system and for a constant current, Eq. (10.13) reduces to

$$\sqrt{\tau} = kAc^0 \quad (10.14)$$

where the constant $k = (nF\sqrt{\pi D})/2I$. In the presence of adsorption, the adsorbed substances that are neither reduced nor oxidized at the electrode block a part of the electrode surface and the result of this blocking is a decrease in available surface area for the electrode reaction (here the deposition of Pb and Sn).

Thus, the surface area A in Eqs. (10.13) and (10.14) must be replaced by the available (free, unoccupied) surface area. This surface area, which is free for the electrode reaction, can be expressed in terms of the surface coverage θ . The fractional surface coverage θ of the electrode surface by an adsorbed substance is defined as

$$\theta = \frac{A_1}{A} \quad (10.15)$$

where A is the total surface area and A_1 the occupied surface area of the electrode. From Eq. (10.15) it follows that the unoccupied surface area A_2 is

$$A_2 = A - A_1 = A(1 - \theta) \quad (10.16)$$

since, from Eq. (10.15), $A_1 = \theta A$.

Finally, the chronopotentiometric equation, for a given system and for constant current, in the presence of adsorption is obtained by substituting A in Eq. (10.14) with A_2 from Eq. (10.16), thus

$$\sqrt{\tau} = kA_2c^0 = kA(1 - \theta)c^0 \quad (10.17)$$

It is seen from Eq. (10.17) that an increase in θ causes a decrease in the transition time τ . If τ_0 is the transition time in the absence, and τ in the presence of adsorption of the electrochemically inactive additives, then the difference

$$\Delta\tau = \tau_0 - \tau \quad (10.18)$$

is a function of the amount of the adsorbed additive. Typical chronopotentiograms for the reduction of Sn^{2+} and Pb^{2+} in both absence and presence of peptone are

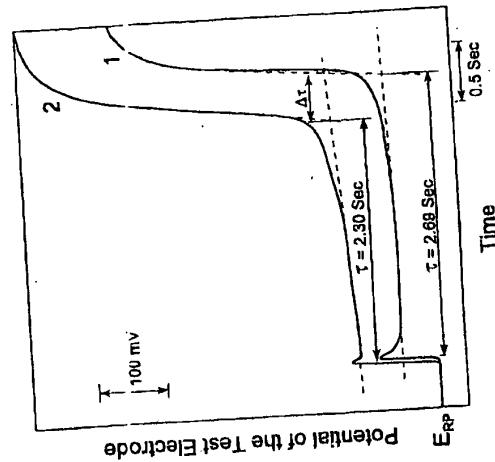


Figure 10.10. Change of transition time for reduction of Pb^{2+} and Sn^{2+} due to adsorption of peptone: 1—chronopotentiogram in the absence of peptone; 2—Chronopotentiogram in the presence of 4 g/L peptone; E_{RP} —the rest potential. (From Ref. 8, with permission from the American Electroplaters and Surface Finishers Society.)

shown in Figure 10.10. At the transition time τ all the available Sn^{2+} and Pb^{2+} ions at the electrode surface are reduced and a new process starts (evolution of hydrogen). The difference $\Delta\tau$ is a function of the bulk concentration of the additive and increases with increasing concentration of the additive according to an adsorption isotherm. Thus, measurements of $\Delta\tau$ can be used to determine concentration or adsorption properties of additives in a solution.

The fractional surface coverage θ can be calculated from the experimental values of τ_0 , τ , and τ_m using the equation

$$\theta = \frac{\tau_0 - \tau}{\tau_0 - \tau_m} \quad (10.19)$$

where τ_m is the transition time for the limiting (saturation) value of adsorption.

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10.4. EFFECT OF ADDITIVES ON KINETICS AND MECHANISM OF ELECTRODEPOSITION

In the discussion of atomistic aspects of electrodeposition of metals in Chapter 6 (Section 6.8), it was shown that in electrodeposition the transfer of a metal ion M^{n+} from the solution into the ionic metal lattice in the electrodeposition process may proceed via one of two mechanisms: (1) direct mechanism in which ion transfer takes place on a kink site of step edge or on any site on the step edge (any growth site) or (2) terrace site ion mechanism. In the terrace site transfer mechanism a metal ion is transferred from the solution (OHP) to the flat face of the terrace region. At this position the metal ion is in adion state and is weakly bound to the crystal lattice. From this position it diffuses on the surface seeking a position with lower potential energy. The final position is a kink site.

Adsorbed additives affect both of these mechanisms by changing the concentration of growth sites c_p on the surface $[n_p/\text{cm}^2]$, (where n_p is the number of growth sites), concentration of adions, c_{ad} on the surface, diffusion coefficient D_{ad} , and the activation energy E_{ad} of surface diffusion of adions.

REFERENCES AND FURTHER READING

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10.5. EFFECT OF ADDITIVES ON NUCLEATION AND GROWTH

In Chapter 7 different growth models were described: layer growth (Section 7.9), nucleation-coalescence growth (Section 7.10), development of texture (Section 7.11), columnar microstructure (Section 7.12), and other structural forms (Section 7.13). In this section we discuss the effect of additives on these growth mechanisms.

Nucleation. In the presence of adsorbed additives the mean free path for lateral diffusion of adions is shortened, which is equivalent to a decrease in the diffusion coefficient D (diffusivity) of adions. This decrease in D can result in an increase in adion concentration at steady state and thus an increase in the frequency of the two-dimensional nucleation between diffusing adions.

Layer Growth. In Chapter 7 (Section 7.9) we showed that many monoatomic steps can unite (bunch, coalesce) to form polyatomic steps in the presence of impurities. Additives can also influence the propagation of microsteps and cause bunching and formation of macrosteps.

Dependence of Types of Deposit on the Surface Coverage by Additive. Type of deposit obtained at constant current density may depend on the value of the surface coverage θ by an additive. Damjanovic et al. (2) studied the effect of various values of the surface coverage θ of n -decylamine on the growth form of copper on the (100) plane of copper single crystal at 5 mA/cm². The surface coverage θ was varied by addition of a known amount of n -decylamine to a highly purified solution of CuSO_4 , H_2SO_4 , and H_2O . The coverage θ of n -decylamine was estimated from the adsorption isotherm for n -decylamine on copper in 1 N NaClO_4 (Fig. 10.4).

It was found that when $\theta < 10^{-2}$ (at the bulk concentration of n -decylamine

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(21)Application number : 09-123160

(71)Applicant : JAPAN STORAGE BATTERY CO
LTD

(22)Date of filing : 24.04.1997

(72)Inventor : MUKASA TOMONORI
ONARI MASAHIKO

(54) LEAD-ACID BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To maintain a stable battery performance over a long term by using a negative electrode activation material containing fatty acid added within a specific range, and specifying the added fatty acid as stearic acid or the salt thereof.

SOLUTION: A drop in the discharge capacity of high efficiency particularly increases according to an increase in the amount of added fatty acid and greatly increases, when the added amount exceeds 2%. Thus, the added amount is kept at 1% or less. A battery added with 0.05% or more of fatty acid loses little amount of liquid, showing an excellent liquid losing characteristic. These results show that the added amount of fatty acid is preferably 0.05% to 1%. The liquid losing characteristic is improved because hydrogen generating reaction is suppressed during overcharging by forming a fatty acid film on an active material surface, thereby raising hydrogen overvoltage and reducing a charge current for constant voltage charge. The fatty acid to be used is zinc stearate and higher fatty acid hardly dissolving into dilute sulfuric acid is preferable as the fatty acid. Particularly, stearic acid and the salt thereof are preferable.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The liquid type lead accumulator characterized by using the negative-electrode active material which is the liquid type lead accumulator which degases these groups of electrode in a battery case by pouring in and energizing a predetermined dilute sulfuric acid on a cell after producing a cell using positive [non-degassed] and a negative-electrode board, and which is manufactured by the so-called battery-case Chemicals method, and by which the fatty acid was added.

[Claim 2] The lead accumulator according to claim 1 characterized by the addition of a fatty acid being 0.05 - 1 % of the weight.

[Claim 3] The lead accumulator according to claim 1 or 2 characterized by the fatty acid to add being stearin acid or its salt.

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MEANS

[Means for Solving the Problem] By pouring in and energizing a predetermined dilute sulfuric acid on a cell, after producing a cell using positive [non-degassed] and a negative-electrode board In the liquid type lead accumulator which degases these groups of electrode in a battery case and which is manufactured by the so-called battery-case Chemicals method the first invention It is characterized by using the negative-electrode active material by which the fatty acid's was added, and third invention is characterized by the fatty acid to add being stearin acid or its salt to ** characterized by the addition of a fatty acid being 0.05 - 1wt% for the second invention.

[0006]

[Embodiments of the Invention] After the liquid type lead accumulator by this invention produces a cell using positive [non-degassed] and a negative-electrode board, by pouring in and energizing a predetermined dilute sulfuric acid on a cell, it is a liquid type lead accumulator which degases these groups of electrode in a battery case and which is manufactured by the so-called battery-case Chemicals method, and is characterized by using the negative-electrode active material by which the fatty acid was added. In addition, although addition of a fatty acid was added when it carried out kneading production of the negative-electrode paste, as an addition, 0.05 - 1wt% is desirable. Stearin acid comparatively cheap as a kind of fatty acid or its salt is desirable.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to improvement of a liquid type lead accumulator.

[0002]

[Description of the Prior Art] The liquid type lead accumulator is used including the object for starting / lighting of an automobile for many uses, such as objects for electric vehicles for dc-battery fork lift trucks etc., and an object for deferment. In recent years, various improvement is advanced, in order that a lead accumulator may suppress the self-discharge under neglect, and in order to reduce the water refilling operation accompanying electrolytic-solution (dilute sulfuric acid) decomposition in use. As the typical thing, reduction of the antimony addition in a positive-electrode grid alloy or adoption of the positive-electrode grid made from a lead alloy (lead-calcium-tin system alloy) which does not contain antimony is mentioned.

[0003] In the case of the lead accumulator for automobiles, the temperature in the engine room in which the lead accumulator is installed becomes 70 degrees C or more at summer. Under such an elevated temperature, there was very much **** by the electrolytic-solution decomposition under overcharge of a battery (moisture solution), and it was inadequate for suppressing increase of low water loss just to advance the so-called above reduction in antimony or antimony free-ization.

[0004]

[Problem(s) to be Solved by the Invention] Then, the technical problem of this invention is improving the fall of the low water consumption of the lead accumulator used under an elevated temperature.

[0005]

[Means for Solving the Problem] By pouring in and energizing a predetermined dilute sulfuric acid on a cell, after producing a cell using positive [non-degassed] and a negative-electrode board In the liquid type lead accumulator which degases these groups of electrode in a battery case and which is manufactured by the so-called battery-case Chemicals method the first invention It is characterized by using the negative-electrode active material by which the fatty acid's was added, and third invention is characterized by the fatty acid to add being stearin acid or its salt to ** characterized by the addition of a fatty acid being 0.05 - 1wt% for the second invention.

[0006]

[Embodiments of the Invention] After the liquid type lead accumulator by this invention produces a cell using positive [non-degassed] and a negative-electrode board, by pouring in and energizing a predetermined dilute sulfuric acid on a cell, it is a liquid type lead accumulator which degases these groups of electrode in a battery case and which is manufactured by the so-called battery-case Chemicals method, and is characterized by using the negative-electrode active material by which the fatty acid was added. In addition, although addition of a fatty acid was added when it carried out kneading production of the negative-electrode paste, as an addition, 0.05 - 1wt% is desirable. Stearin acid comparatively cheap as a kind of fatty acid or its salt is desirable.

[0007]

[Example] Hereafter, this invention is explained based on an example.

[0008]

[Example 1] The positive-electrode grid made from a Pb-Sb system alloy (1.7%Sb) and the negative-electrode grid made from an Pb-calcium-Sn system alloy were filled up with positive [for lead accumulators], and the negative-electrode paste, respectively, digestion and dryness were given, and the non-degassed positive/negative plate was obtained. In addition, the negative-electrode paste used here was produced as follows.

[0009] Proper quantity addition of a barium sulfate, a ligninsulfonic acid, and the carbon black was carried out at the ball mill formula lead powder, and after dry blending, the water of the specified quantity and the dilute sulfuric acid of specific gravity 1.4 were supplied one by one, and it kneaded. As an amount of barium sulfates, 0.05 - 2% can be used as an amount of carbon 0.05 to 1% as an amount of ligninsulfonic acids 0.1% to 2%. Then, eight kinds of pastes which add a fatty acid 0 to 5% to this paste, knead again, and are shown in Table 1 were produced. In addition, weight % to a lead powder shows each of these additions.

[0010] The cell was assembled combining these positive/negative plates, the dilute sulfuric acid of the specified quantity was poured in, battery-case Chemicals was given, and the liquid type lead accumulator of =1-8 shown in Table 2 was obtained. It united and the cell (= in Table 2 9-16) which assembled the cell using the type Chemicals finishing plate for ** which gave rinsing and dryness after carrying out tank formation of positive [above] and the negative-electrode board in the dilute sulfuric acid of specific gravity 1.05 beforehand, poured in the predetermined dilute sulfuric acid, and performed the initial charge was also produced for comparison. Each of these cells is nominal capacity 48Ah(s) (5 hour rate) and the type lead accumulators for [nominal-voltage 12 / 55D23] the automobiles of V which were indicated by JIS D 5301.

[0011]

[Table 1]

負極板記号	脂肪酸添加量 (%)
A	0
B	0.05
C	0.1
D	0.2
E	0.5
F	1
G	2
H	5

[Table 2]

電池No	負極板記号	脂肪酸添加量 (%)	化成方法	備考
1	A	0	電槽化成	従来品
2	B	0.05		本発明品
3	C	0.1		
4	D	0.2		
5	E	0.5		
6	F	1		
7	G	2		比較品
8	H	5		
9	A	0	タンク化成	従来品
10	B	0.05		
11	C	0.1		
12	D	0.2		
13	E	0.5		
14	F	1		
15	G	2		
16	H	5		

Next, 5 hour-rate service capacity (25 degrees C) and high-rate-discharge capacity (300A, -15 degree C) of these cells were investigated, and 75-degree-CJIS light load life test was presented. In addition, although the examination was performed according to JIS D 5301, temperature of light load life test was raised and carried out at 75 degrees C here. Moreover, the weight of a cell was measured during light load life test, and it investigated about the low water loss in a cycle.

[0012] The low water loss under 5 hour-rate service capacity of these cells, the high-rate-discharge persistence time, and life test (average low water loss per 1 cycle charge and discharge) is shown in Table 3. Although the addition of a fatty acid was practically equal to 5 hour-rate service capacity when it was 1% or less, the fall of high-rate-discharge capacity became large, and they fell [the fall] greatly at 2% or more especially as the addition of a tank coal chemical product [a battery-case coal chemical product and] of a fatty acid increased. therefore, you should carry out an addition to 1% or less -- ** -- it thinks Moreover, the cell (=2-8) which added the fatty acid 0.05% or more in the battery-case coal chemical product had little low water loss under life test compared with elegance conventionally, and

the outstanding low water consumption was shown. From these results, the addition of a fatty acid is considered to be what has 0.05 - 1 desirable%.

[0013]

[Table 3]

電池 No	脂肪酸添 加量(%)	化成方法	備考	5時間率放 電容量(Ah)	高率放電持 続時間(分)	減液量 (g/91%)
1	0	電槽化成	従来品	50.2	2.8	0.435
2	0.05		本発明品	50.2	2.8	0.382
3	0.1			50.0	2.7	0.365
4	0.2			49.9	2.6	0.360
5	0.5			49.1	2.3	0.356
6	1			48.5	2.0	0.352
7	2		比較品	47.2	1.5	0.308
8	5			45.5	0.9	0.280
9	0	タンク 化成	従来品	49.8	2.5	0.450
10	0.05			49.6	2.5	0.415
11	0.1			49.5	2.4	0.403
12	0.2			49.2	2.3	0.397
13	0.5			48.9	2.1	0.394
14	1			48.0	1.8	0.390
15	2			46.5	1.3	0.370
16	5			45.1	0.8	0.356

By forming the coat of a fatty acid in an active material front face, it is made hard to happen the hydrogen generating reaction under overcharge, a hydrogen overvoltage goes up, and it is considered because the charging current in constant-potential charge was reduced that low water consumption improved by addition of the fatty acid to a negative-electrode active material.

[0014] Although there is much low water loss of the tank coal chemical product (=10-16) which added the fatty acid compared with this invention article, it is considered because some fatty acids eluted and disappeared from the negative-electrode active material at the time of tank Chemicals or rinsing after Chemicals.

[0015] In addition, about the life performance of these cells, each was 5500 to 6500 cycle and it was practically equal.

[0016] Although the fatty acid used here was a zinc stearate, even if it used the palmitic acid, the lauric acid, and the myristic acid, it had the same effect. The higher fatty acid to which the dissolution to a dilute sulfuric acid cannot start a fatty acid easily is desirable, and especially stearin acid and its salt are desirable.

[0017] Moreover, it is not added in order to prevent oxidization of the negative-electrode active material (spongy metal lead) after Chemicals and rinsing / dryness (vacuum drying) among the atmosphere, and the stearin acid used as an active material additive of the conventional negative-electrode board for tank Chemicals is not used for the purpose of improvement in low water consumption like this invention. Therefore, the technology of above-mentioned tank Chemicals is not related to this invention at all, not using a fatty acid as a negative-electrode active material additive for battery-case Chemicals in the former.

[0018]

[Effect of the Invention] As mentioned above, it is the liquid type lead accumulator manufactured by the battery-case Chemicals method according to this invention as the example described, and the industrial value -- the liquid type lead accumulator characterized by using the negative-electrode active material which added a fatty acid or its salt can maintain the cell performance by which **** in use under an elevated temperature could not happen easily, and was stabilized for a long period of time -- becomes size.

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TECHNICAL FIELD

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PRIOR ART

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EXAMPLE

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[0011]

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[0014] Although there is much low water loss of the tank coal chemical product (=10-16) which added the fatty acid compared with this invention article, it is considered because some fatty acids eluted and disappeared from the negative-electrode active material at the time of tank Chemicals or rinsing after Chemicals.

[0015] In addition, about the life performance of these cells, each was 5500 to 6500 cycle and it was practically equal.

[0016] Although the fatty acid used here was a zinc stearate, even if it used the palmitic acid, the lauric acid, and the myristic acid, it had the same effect. The higher fatty acid to which the dissolution to a dilute sulfuric acid cannot start a fatty acid easily is desirable, and especially stearin acid and its salt are desirable.

[0017] Moreover, it is not added in order to prevent oxidization of the negative-electrode active material (spongy metal lead) after Chemicals and rinsing / dryness (vacuum drying) among the atmosphere, and the stearin acid used as an active material additive of the conventional negative-electrode board for tank Chemicals is not used for the purpose of improvement in low water consumption like this invention. Therefore, the technology of above-mentioned tank Chemicals is not related to this invention at all, not using a fatty acid as a negative-electrode active material additive for battery-case Chemicals in the former.

[Translation done.]



001799586/7

DIALOG(R) File 351:DERWENT WPI

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001799586

WPI Acc No: 77-20553Y/197712

Alkaline battery (dis)charge improving agent - of quaternary ammonium salt contg. benzyl gp. added to anode mass and /or electrolyte

Patent Assignee: MATSUSHITA ELEC IND CO LTD (MATU)

Number of Countries: 001 Number of Patents: 001

Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Main IPC	Week
JP 50091728 A		19750722					197712 B

Priority Applications (No Type Date): JP 73143154 A 19731219

Abstract (Basic): JP 50091728 A

Benzyl group-contg. quat. ammonium salt is added to anode active mass and/or electrolytes in alk. batteries. The additive improves the charging and discharging characteristics of batteries and extends their service life.

For example, 3.0% dodecyldimethylbenzylammonium chloride was added to a Ni-Zn alk. battery electrolyte (30% KOH). The service life of the battery was by a factor of >2 greater than that of a battery without the additive.

Derwent Class: E14; L03; X16

International Patent Class (Additional): H01M-000/00

?t001591872

JP 50-091 728 :



⑩ 日本国特許庁
公開特許公報

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⑮日本分類

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H01M 4/36

特 許 願 (21)

昭和 48 年 12 月 19 日

特許庁長官殿

1 発明の名称

アルカリ電池

2 発明者

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(ほか1名)

5 送付書類の目録

(1) 明 細 書 1 通
(2) 図 面 1 通
(3) 発 任 状 1 通
(4) 願 書 副 本 1 通



明 細 書

1. 発明の名称

アルカリ電池

2. 特許請求の範囲

負極活性物質もしくはアルカリ電解液または両者にベンゾル基を有する第4級アミンを含有させたことを特徴とするアルカリ電池。

3. 発明の詳細な説明

本発明は、負極活性物質に鉄、カドミウム、亜鉛を用い、電解液にアルカリ溶液を用いるアルカリ電池に関するもので、充放電特性の向上を目的とするものである。

従来からアルカリ電池の負極活性物質として、鉄、カドミウム、亜鉛などが用いられてきたが、近年、低公害性、高エネルギー密度、かつ、構造安価なとことなどから再び亜鉛が注目を集めている。鉄は水素過電圧が低く、カドミウム、亜鉛は特に、充電の際、発現する樹枝状結晶の抑止が困難なために充電が容易でなく寿命が短い欠点がある。特に放電の際電解液中に析出したカドミウムや亜鉛が、

充電によって電極基体上に電着されるときアンパライト状に析出しやすく、対極に向かって成長し、正負極間に介在するセパレータを通して正極と短絡して短絡したり、あるいは樹枝状によって負極が損傷されて、電池性能が著しく低下する原因となっていた。

この欠点を解消する目的で負極活性物質あるいはアルカリ電解液中に鉄、銅化合物を添加して、充電の際の亜鉛 dendritic の成長を抑止することが提案された。しかしながらこれらはいずれも金属被膜を形成し、金属負極表面を覆うために金属放電の繰返電利用率が低下することから、添加量は極度に制限されるという欠点があった。

本発明は負極活性物質もしくはアルカリ電解液または両者にベンゾル基を有する第4級アミンを添加することにより、放電反応を抑制することなく充電の際の樹枝状結晶を抑止すると同時に水素過電圧を増加させ、電池の充放電特性の向上を図るものである。

以下、本発明を特に樹枝状結晶の発現が顕著で

ある塩類を負極活性物質とするニッケル-亜鉛アルカリ電池に適用した例を説明する。

第1図はニッケル-亜鉛アルカリ電池の一部の断面図である。図において1は銅製ニッケルからなる正極板、2は酸化亜鉛粉末100重量部と長さ2〜3mmのポリプロピレン繊維0.5重量部との混合体に2.5%のポリビニルアルコール水溶液40重量部を注入して、練合したペーストを塗布した板ネットに電着乾燥した後、初底で包被した負極板であり、正極板1と負極板2には可溶性の硫酸ポリ塩化ビニル管で外周を密封した正極および負極リード3、4が各々取り付けられている。正、負両極のリード3、4は正極および負極端子5、6に各々一端が接続されている。7はセパレータで、亜鉛負極2枚を各々セルルーム状構造で一室をなし、次いでセロファン紙で二室をなし、これをU字形に折りまげて負極板2を完全に包被している。このセパレータで包被された負極板の両側に正極板1を挿入し、交互に正、負両極板が充満するように亜鉛液が構成されている。図に

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示すものは正極板5枚、負極板4枚からなっている。8、9はポリスチレン系の合成樹脂からなる電極と集電、集電には銅板を内蔵した集電口10が取り付けられている。

第2図は次の表に示す構成からなる公称3AHの亜鉛放電用電池の充放電特性を示したものである。ここで充放電率は、1サイクルごとに0.4%で放電容量の150%を充電電流で充電したのち、毎回完全放電を行うものである。なお、電解液は30%のKOH水溶液である。

電極記号	添加剤	亜鉛除板	電解液
A	ドデシルジ(ヒドロキシエチル)メチル	0.05wt%	0
B	アンモニウムクロライド	0.5 wt%	0
C	同上	0	0.1 wt%
D	同上	0	5.0 wt%
E	ドデシルリメチルアンモニウム-	0.05wt%	0
F	クロライド	0.5 wt%	0
G	同上	0	0.1 wt%
H	同上	0	5.0 wt%
I	ドデシルジ(メチル)ベンジル-	0.08wt%	0
J	アンモニウムクロライド	0.5 wt%	0

K	ドデシルジ(メチル)ベンジル-	0	0.1 wt%
L	アンモニウムクロライド	0	5.0 wt%
M	同上	0.05wt%	5.0 wt%
N	同上	0	5.0 wt%
O	無添加	0	0

図に示した有機添加剤は全て第4級アミン類である。電池A〜Dは全て近い放電容量を示し、電池E〜Hは無添加の電池Oとほとんど同じでいづれも大きな効果はないのに対して、電池I〜Nのみが著しく長寿命であり添加量に比例して寿命は長くなり貯蔵添加量も大きい。添加剤が全て第4級アミン類であるにもかかわらず電池寿命が著しく異なる原因は、塩基原子に結合するアルキル基や官能基に起因する特異効果により説明できる。亜鉛負極の充放電反応における各々の添加剤の吸着挙動を定量的に分析した結果、ドデシルジ(ヒドロキシエチル)メチルアンモニウムクロライドは充電時よりもむしろ放電時に亜鉛に吸着して、亜鉛の放電反応を抑制するため放電利用率は低

下し、製造しないため寿命は短くなる。これに比べてドデシルリメチルアンモニウムクロライドとドデシルジ(メチル)ベンジルアンモニウムクロライドは充電時、亜鉛に吸着し、放電時には脱離する傾向がみられるが、吸着は前者に比べ水素過電圧が高く、充電時水素サイトに吸着し、同時にデンドライトの成長を著しく抑制する効果を示す。また、放電の際には脱離する傾向にあることから、亜鉛サイトに吸着したいと考えられる。充放電サイクル初期に無添加の場合に比べ、低い放電容量を示すのは、平滑電析効果により亜鉛の反応面積が一時的であるためである。貯蔵容量は、電解液量1位あたり0.0008%から0.2%であり、これ以上添加するとニッケル正極に対して悪影響がみられる。しかしながら空電極を用いる場合は、2倍の貯蔵容量がある。また、負極活性物質中に添加する場合は、1%あたり0.0008%〜0.2%である。

以上のことから第4級アミン類の中でもベンジル基を有するドデシルジ(メチル)ベンジルアン

モニウムクロライドは高純度の長寿命化に著しく有効であることは明白である。またペンシル炭のエンレーン量の数が0-9の場合、同様に有効であり、ペンシル炭の数が1-9の場合有効である。陰素原子に結合する官能基が4番ともペンシル炭に吸着されると若干吸着力は立体障害等により弱くなるため効果は弱くなる。総じて、ペンシル炭を含む第4族アミンは亜鉛、カドミウム、鉄などに吸着し、水素還元電圧を高くし、腐蝕性腐食を著しく抑制し、電池の長寿命化に有効である。これらの第4族アミンの水酸化物、臭化物、過化物、硫酸塩は特に有効である。電解液としては、 KOH 、 LiCl 、 NaOH あるいはそれらの混合組成の比率いかんを問わず有効である。

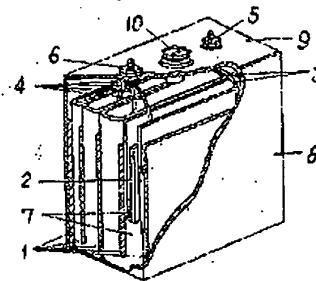
4. 図面の簡単な説明

第1図は本発明の実施例におけるニッケル-亜鉛アルカリ電池の一部欠断面構造。第2図は同電池の充放電特性を示す図である。

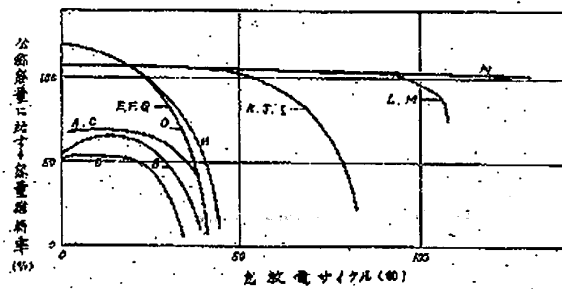
1.....正極、2.....負極、7.....セパレータ。

代理人の氏名 弁護士 中 尾 敏 彦 氏 4名

第 1 図



第 2 図



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SEALED LEAD-ACID BATTERY

Patent number: JP1267965
Publication date: 1989-10-25
Inventor: NITTA EIJI
Applicant: JAPAN STORAGE BATTERY CO. LTD
Classification:
- international: H01M10/06; H01M4/68; H01M10/08
- european:
Application number: JP19880096364 19880419
Priority number(s):

Abstract of JP1267965

PURPOSE: To improve the recovery charging characteristic and provide a trait to sustain with overdischarge and being left as it is for a long time, by adding quaternary ammonium ions.

CONSTITUTION: With co-existence of quaternary ammonium having common ion as SO_4 , a weak electrolytic PbSO_4 reduces its electric dissociativeness, and the concentration of Pb^{2+} is suppressed. That is, the electric dissociativeness (concentration of Pb^{2+}) of PbSO_4 is invertedly proportional to the concentration of the quaternary ammonium ions added. Accordingly admission of charging is improved by adding tetraethyl-ammonium ions or tetramethyl-ammonium ions as quaternary ammonium ion to the electrolyte. Even under long-term left condition charge condition, existence of the quaternary ammonium ion has good effect.

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 63-096364

(71)Applicant : JAPAN STORAGE BATTERY CO
LTD

(22)Date of filing : 19.04.1988

(72)Inventor : NITTA EIJI

(54) SEALED LEAD-ACID BATTERY

(57)Abstract:

PURPOSE: To improve the recovery charging characteristic and provide a trait to sustain with overdischarge and being left as it is for a long time, by adding quaternary ammonium ions.

CONSTITUTION: With co-existence of quaternary ammonium having common ion as SO, a weak electrolytic PbSO₄ reduces its electric dissociativeness, and the concentration of Pb²⁺ is suppressed.

That is, the electric dissociativeness (concentration of Pb²⁺) of PbSO₄ is ~~invertedly~~ proportional to the concentration of the quaternary ammonium ions added. Accordingly admission of charging is improved by adding tetraethyl-ammonium ions or tetramethyl-ammonium ions as quaternary ammonium ion to the electrolyte. Even under long-term left condition and charge condition, existence of the quaternary ammonium ion has good effect.

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⑪ 特許出願公開

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A-6821-5H
7239-5H

審査請求 未請求 請求項の数 1 (全3頁)

⑮ 発明の名称 密閉形鉛蓄電池

⑯ 特 願 昭63-98364

⑰ 出 願 昭63(1988)4月19日

⑱ 発 明 者 新 田 英 次 京都府京都市南区吉祥院西ノ庄猪之馬場町1番地 日本電池株式会社内

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明 細 書

1. 発明の名称

密閉形鉛蓄電池

2. 特許請求の範囲

1. 鉛-カルシウム-錫合金または鉛-カルシウム-鉛-アルミニウム合金を正極格子に用いると共に、電解液に第4アンモニウムイオンを含む密閉形鉛蓄電池。

3. 発明の詳細な説明

産業上の利用分野

本発明は密閉形鉛蓄電池の改良に関するものである。

従来の技術とその課題

密閉形鉛蓄電池は電解液が外部に漏れないのでポータブル電子機器の小容量電源として広く普及している。近年密閉形鉛蓄電池は小型軽量化や高性能化が進み、限られたスペース内により多くの活物質を入れる必要に迫られて、1セル当たりの活物質量に対する硫酸量の割合が小さくなってきている。したがって過放電または長期放置による自

放電などの原因により電解液比重の著しい低下を生じる。電解液中の硫酸濃度(比重)が低下すると、極板中に生成した硫酸鉛は次の表に見ることく、硫酸濃度の低下と共に溶解度が大きくなり、特に硫酸が著しく少ない領域では激増する。

硫酸濃度 (wt%)	硫酸鉛の溶解度 (mg/g)
0	45.2
0.5	4.60
1	4.91
5	6.15
10	6.68
20	5.18
25	3.76
30	2.75
35	2.02
40	1.52

その後の周囲温度の変化や充電などのために硫酸鉛の比較的大きな結晶や粗の針状結晶が極板表面に析出する。このように充電しても元に戻らない結晶性硫酸鉛が生成すると、再充電が困難にな

り、電池容量や放電電圧が低下したり、また鉛の針状結晶生成はセパレータを貫通して内部短絡の原因となっていた。

これらの欠点を解消する目的で硫酸ナトリウムや硫酸カリウムなどのアルカリ金属の硫酸塩や硫酸アンモニウムなどの添加による改良が試みられているが、アルカリ金属の場合は、添加量が少ないと効果に乏しく、また多量に添加すると蓄電池の内部抵抗の増加、活性物質細孔内への電解液の浸透力の低下、電解液中の水素イオン濃度の減少などにより容量や放電電圧の低下をもたらす欠点があった。また硫酸アンモニウムの添加はアンモニウムイオン(NH₄⁺)が酸化を受けやすく、酸化によりH₂O₂やH₂O₂を生じ、格子の腐食やシャトル作用により自己放電を促進したり、さらに硫酸アンモニウムは弱過酸化性のため電離度が小さくPb²⁺の生成を抑制する効果に乏しいものであった。

課題を解決するための手段

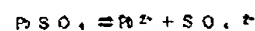
本発明は電解液に対し溶解度が大きく、かつ電

離度が著しく大きい第4アンモニウムイオンを添加することにより上記欠点を解消した密閉形鉛蓄電池を提供するもので、水酸化第4アンモニウムイオンは電子構造から見て水酸化ナトリウムや水酸化カリウムに相当する塩基性をもっている。

作用

この第4アンモニウムイオンを電解液に添加することによる作用は分析化学で共通イオン効果と呼ばれているもので、その原理を電解液中のPb²⁺の濃度について略述する。

いま、PbSO₄ 1モルが単独に溶液中にあると、その電離度を α' とすれば、PbSO₄、Pb²⁺、SO₄²⁻のそれぞれはつぎのように分配する。



$$1 - \alpha' \quad \alpha' \quad \alpha'$$

この反応の平衡定数K_{pb}は[Pb²⁺][SO₄²⁻]/[PbSO₄] = $\alpha'^2 / (1 - \alpha')$ で表わされ、 α' の大きさは 1×10^{-4} g/度程度で、したがってPbSO₄はほとんど1と見なすことができる。

$$K_{pb} = \alpha'^2 / (1 - \alpha')$$

$$= \alpha(\alpha + \beta) / (1 - \alpha)$$

$$1 - \alpha' = 1 - \alpha = \beta + 1 \text{ なので、}$$

$$\alpha'^2 = \alpha^2 + \alpha, \text{ したがって } \alpha' > \alpha$$

すなわち弱電解質のPbSO₄はSO₄²⁻という共通イオンを持つ第4アンモニウムが共存するとその電離度が小さくなり、Pb²⁺の濃度は小さく抑えられる。

PbSO₄と第4アンモニウム塩の濃度をそれぞれC_{pb}、C_{ts}とすれば、

$$\text{Pb}^{2+} \text{ の濃度 } [\text{Pb}^{2+}] = \alpha C_{pb}, \text{ SO}_4^{2-} \text{ イオン濃度 } [\text{SO}_4^{2-}] = \alpha C_{pb} + \beta C_{ts}, \text{ PbSO}_4 \text{ 濃度 } [\text{PbSO}_4] = (1 - \alpha) C_{pb}$$

$$K_{pb} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] / [\text{PbSO}_4]$$

$$= \alpha C_{pb} (\alpha C_{pb} + \beta C_{ts}) / (1 - \alpha) C_{pb}$$

$$1 - \alpha \neq 1, \beta \neq 1 \text{ と考えられるから、}$$

$$K_{pb} = \alpha^2 C_{pb} + \alpha C_{ts}$$

$$1 - \alpha \neq 1, \beta \neq 1 \text{ と考えられるから、}$$

$$K_{pb} = \alpha^2 C_{pb} + \alpha C_{ts}$$

$$\text{極端な場合として } C_{pb} = C_{ts} = C \text{ とすれば、}$$

$$K_{pb} = \alpha(\alpha + 1)C$$

$$\alpha + 1 \neq 1 \text{ とすれば、 } \alpha = K_{pb} / C$$

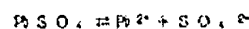
第4アンモニウム(ここでは記号Mで表わす)の硫酸塩1モルが単独に溶液1度中にあるときの電離度を β' とすると



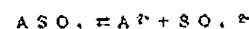
$$1 - \beta' \quad \beta' \quad \beta'$$

硫酸第4アンモニウムは強電解質なので、電離度 β' は大きくほぼ1と見なすことができる。

次に硫酸鉛と硫酸第4アンモニウムが同一溶液に混在している場合を考えると、それらの電離度をそれぞれ α 、 β とすれば各成分の配分は次のようになる。



$$1 - \alpha \quad \alpha \quad \alpha$$



$$1 - \beta \quad \beta \quad \beta$$

第4アンモニウムイオンは鉛のどんなイオンの影響も受けないので充分電離すると考えられ、

$$\beta' \neq \beta \text{ と見なすことができる。}$$

$$[\text{Pb}^{2+}] = \alpha, [\text{SO}_4^{2-}] = \alpha + \beta,$$

$$\text{PbSO}_4 = 1 - \alpha$$

すなわち $PbSO_4$ の電解度(10²¹の濃度)は添加する第4アンモニウムイオンの濃度に反比例することがわかる。

実験例

本発明ははじめに記した鉛電池の欠点を改良するものであり、以下本発明に至った実験の結果を説明する。

第1表に示すごとく電解液に各種添加物を加え5Ahの電池を試し、次の実験を行った。

実験1

20HR電流にて端子間電圧が0Vになるまで放電し、引き続き端子間を短絡して150時間放置し、そのうち2.25V/セルの定電圧で充電を行い、その30分目の電流と5時間目充電電流値を調べる。

実験2

定電流で完全に充電した後、20HR電流にて端子間電圧が0Vになるまで放置し、引き続き端子間を短絡して40℃にても6ヶ月間および12ヶ月間の保存を行い、10HR電流にて定格容量の200%の充電を行い容量の回復率を調べる。結果を第1表に示す。

また、本発明は第4アンモニウム塩単独の添加に限らず磷酸や硫酸などを併用することは何等差支えない。

発明の効果

テトラメチルアンモニウムイオンあるいはテトラエチルアンモニウムイオンを電解液に添加することにより電解液の低比重領域での Pb^{2+} の溶解度を低く抑えて、結晶成長を妨げ、しかも第4アンモニウムイオンの存在により、電解液の電導度を大きく低下させることがないため回復充電特性が改良されると共に、セパレータ貫通ショートもなくなり、過放電や長期放置に耐える電池を提供することができ、その工業的価値は大である。

出願人 日本電池株式会社

す。

第1表

NO.	電解液への添加物 名称	量 g/l	充電電流(mA)		容量回復率(%)	
			30分目	5時間目	6ヶ月目	12ヶ月目
1	—	0	320	280	83	40
2	NH_4SO_4	8	480	468	93	89
3	K_2SO_4	8	480	433	90	83
4	$(NH_4)_2SO_4$	8	400	370	88	75
5	$[N(CH_3)_3]_2SO_4$	2	528	493	100	98
6	$[N(C_2H_5)_3]_2SO_4$	2	523	498	100	97

実験1の結果から、実験方法に示すごとく放置条件及び充電条件では、第4アンモニウムイオンであるテトラメチルアンモニウムイオンやテトラエチルアンモニウムイオンを電解液に添加すれば充電受け入れは従来のものに比べ改善され、しかも添加量が少なくても同様の作用を有することがわかる。実験2の結果から、実験方法に示すように長期放置条件及び充電条件においては第4アンモニウムイオンの存在が有効であることがわかる。また、これらを添加したセルはいずれも放置後の充電で内部短絡を生じるものは見られなかった。

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1 発明の名称

アルカリ電池

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5 送付書類の目録

(1) 明 細 書 1 通
(2) 図 面 1 通
(3) 発 任 状 1 通
(4) 願 書 副 本 1 通



明 細 書

1. 発明の名称

アルカリ電池

2. 特許請求の範囲

負極活性物質もしくはアルカリ電解液または両者にベンゾル基を有する第4級アミンを含有させたことを特徴とするアルカリ電池。

3. 発明の詳細な説明

本発明は、負極活性物質に鉄、カドミウム、亜鉛を用い、電解液にアルカリ溶液を用いるアルカリ電池に関するもので、充放電特性の向上を目的とするものである。

従来からアルカリ電池の負極活性物質として、鉄、カドミウム、亜鉛などが用いられてきたが、近年、安全性、高エネルギー密度、かつ、構造安価なことなどから再び亜鉛が注目を集めている。鉄は水素過電圧が低く、カドミウム、亜鉛は特に、充電の際、発生する腐蝕性物質の抑制が顕著なために充電が容易でなく寿命が短い欠点がある。特に、放電の際電解液中に生成したカドミウムや亜鉛が、

充電によって電極基体上に電着されるときアンパライト状に析出しやすく、対極に向かって成長し、正負極間に介在するセパレータを通して正極と短絡して短絡したり、あるいは短絡によって負極が損傷されて、電池性能が悪しく低下する原因となっていた。

この欠点を解消する目的で負極活性物質あるいはアルカリ電解液中に鉛、銅化合物を添加して、充電の際の亜鉛 dendrite の成長を抑止することが提案された。しかしながらこれらはいずれも金属被膜を形成し、金属負極表面を侵食するために過放電の放電利用率が低下することから、添加量は極度に制限されるという欠点があった。

本発明は負極活性物質もしくはアルカリ電解液または両者にベンゾル基を有する第4級アミンを添加することにより、放電反応を抑制するとなく充電の際の腐蝕性物質を抑止すると同時に水素過電圧を増加させ、電池の充放電特性の向上を図るものである。

以下、本発明を特に腐蝕性物質の発生が顕著で

ある連絡を負極活性物質とするニッケル-亜鉛アルカリ電池に適用した例を説明する。

第1図はニッケル-亜鉛アルカリ電池の、図1欠解図解である。図にかいて1は銅板ニッケルからなる正極板、2は酸化亜鉛粉末の重量部と長さ2〜3mmのポリアミド半膜部、3は重量部との混合体に2,5gのポリビニルアルコール水溶液の重量部を混入して、練合したペーストを塗または銅ネットに塗布乾燥した後、和紙で包被した負極板であり、正極板1と負極板2には可溶性の電解液が酸化ビニル管で外周を包被した正極および負極リード3、4が各々取り付けられている。正、負両極のリード3、4は正極および負極端子5、6に各々一端が接続されている。7はセパレータで、正極負極2枚を各々セルケースに収容して一室をなし、次いでセロファン紙で二室をなし、これをU字状に折りまげて負極室2を完全に包被している。このセパレータで包被された負極室の両側に正極板1を挿入し、交互に正、負両極板が充満するように電解液が構成されている。図に

K	ドデシルジ(メチル)ベンジル-	0	0.1 wt%
L	アンモニウムクロライド	0	3.0 wt%
M	同 上	0.05 wt%	3.0 wt%
N		0	3.0 wt%
O	無 添 加	0	0

図に示した有機添加剤は全て第4級アミン類である。電池A〜Dは全て近い放電容量を示し、電池E〜Hは無添加の電池Oとほとんど同じでいずれも大きな効果はないのに対して、電池I〜Nのみが著しく長寿命であり添加量に比例して寿命は長くなり許容添加量も大きい。添加剤が全て第4級アミン類であるのにもかかわらず電池寿命が著しく異なる原因は、電解液に結合するアルカリ基や官能基に起因する特殊効果により説明できる。亜鉛負極の充放電反応における各々の添加剤の吸着挙動を定量的に分析した結果、ドデシルジ(ヒドロキシエチル)メチルアンモニウムクロライドは充電時よりもむしろ放電時に強く吸着して、亜鉛の放電反応を抑制するために放電利用率は低

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示すものは正極板5枚、負極板4枚からなっている。8、9はポリスチレン系の合成樹脂からなる電槽と蓋で、蓋9には排気弁を内蔵した真空口10がとりつけられている。

第2図は次の表に示す構成からなる公称8AHの高率放電用電池の充放電特性を示したものである。ここで充放電特性とは、1サイクルごとに0.4Aで放電容量の1.60倍を定電流充電したのち、毎回完全放電を行うものである。なお、電解液は30gのKOH水溶液である。

電池 記号	添 加 剤	定電流放電	電 解 液
A	ドデシルジ(ヒドロキシエチル)メチル	0.05 wt%	0
B	アンモニウムクロライド	0.5 wt%	0
C	同 上	0	0.1 wt%
D		0	3.0 wt%
E	ドデシルジメチルアンモニウム-	0.05 wt%	0
F	クロライド	0.5 wt%	0
G	同 上	0	0.1 wt%
H		0	3.0 wt%
I	ドデシルジ(メチル)ベンジル-	0.05 wt%	0
J	アンモニウムクロライド	0.5 wt%	0

下し、製造しないために寿命は短くなる。これに比べてドデシルジメチルアンモニウムクロライドとドデシルジ(メチル)ベンジルアンモニウムクロライドは充電時、亜鉛に吸着し、放電時には脱着する傾向がみられるが、前者は前者に比べ水素過電圧が高く、充電時水素サイトに吸着し、同時にデンドライトの成長を著しく抑制する効果を示す。また、放電の際には脱着する傾向にあることから、亜鉛サイトに吸着したいと考えられる。充放電サイクル初期に無添加の場合に比べ、低い放電容量を示すOは、予備電析効果により亜鉛の反応面積が一時的であるためである。許容添加量は、電解液量1あたり0.0003gから0.2gであり、これ以上添加するとニッケル正極板に対して吸着がみられる。しかしながら亜鉛電極を用いる場合は、2倍の許容量がある。また、負極物質中に添加する場合は、1gあたり0.0003g〜0.2gである。

以上のことから第4級アミン類の中でもベンジル基を有するドデシルジ(メチル)ベンジルアン

モリウムクロライドは高効率の長寿命化に著しく有効であることは明白である。またベンジル基のニッケレン数の数が0-2の場合、同様に有効であり、ベンジル基の数が1-3の場合有効である。陰極原子に結合する官能基が4個ともベンジル基に置換されると若干の電圧は立体的障害等により弱くなるため効果は弱くなる。総じて、ベンジル基を有する第4級アミンは炭素、カドミウム、鉄などに吸着し、水素還元電圧を高くし、析出状物を著しく抑制し、電池の長寿命化に有効である。これらの第4級アミンの水酸化物、臭化物、塩化物、硫酸塩は毎式有効である。電解液としては、 KOH 、 LiOH 、 NaOH あるいはそれらの混合組成の比率いかんを問わず有効である。

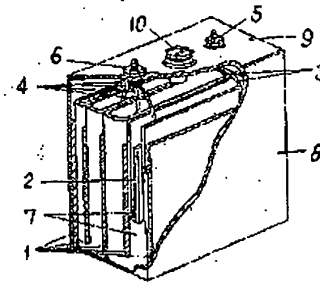
4. 図面の簡単な説明

第1図は本発明の実施例に於けるニッケル-亜鉛アルカリ電池の一部欠断面図。第2図は同電池の充放電特性を示す図である。

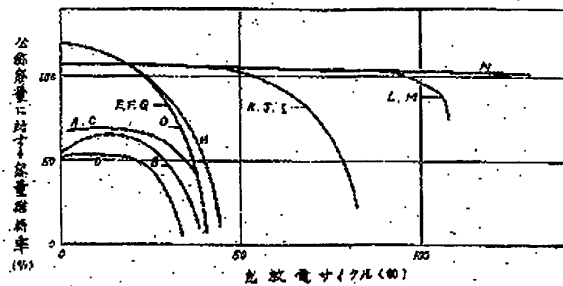
1.....正極、2.....負極、T.....セパレータ。

代理人の氏名 弁護士 中 尾 敏 彦 氏 1名

第 1 図



第 2 図



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